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THE VAPOR PRESSURE OF HCL - WATER SOLUTIONS BELOW 0C.(U)
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"A School of Mineral Resources"
UNIVERSITY OF NEVADA, RENO
RENO, NEVADA 89557

Department of Chemical & Metallurgical Engineering

LEVEL II

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September 1978

Interim Report; Covering Period 1 May 77 to 31 Aug 78

THE VAPOR PRESSURE OF HCL - WATER SOLUTIONS BELOW 0C

Prepared by: E. Miller

Work Performed by: E. Miller

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Prepared for: AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (NA)
Building 410
Bolling AFB, D.C. 20332
Attention: Dr.J.F. Masi

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ABSTRACT

An experimental study has been initiated to measure the equilibrium vapor pressures of solutions of hydrochloric acid at temperatures from 0 to -55C. Total vapor pressure data and calculated heat of vaporization values are reported for 19.9 wt pct and 36.0 wt pct solutions at temperatures of 0 to -40C. Measured vapor pressures at 0C agree with values reported by previous investigators. Total vapor pressures and partial pressures of 0 - 42 wt pct hydrochloric acid liquid and solid solutions from 0 to -55C are planned for the next contract period.

INTRODUCTION

The vapor pressure in equilibrium with hydrogen chloride solutions is important to physical chemists and thermodynamicists interested in the behavior of strong electrolytes. Since hydrochloric acid is a primary chemical used in the chemical and metallurgical industries, it has practical significance as well. Recently, the US Air Force and the other Services have emphasized the development of smokeless solid propellants for tactical rocket applications. One major class of propellants for such applications incorporates ammonium perchlorate oxidizer. The combustion products from these propellants characteristically include quantities of water and hydrogen chloride gases which upon condensing produce a cloud of secondary smoke. The presence of such smoke causes interference with optical guidance systems, obscures the target, and produces a visible signature which reduce the effectiveness of the rocket system. Efforts are underway at several DOD agencies to experimentally define the environmental conditions under which smoke is produced for a given propellant, and in a parallel effort to predict theoretically the environmental conditions for the appearance of smoke in the rocket plume. Basic to these studies are data defining the equilibrium vapor pressures of HCl and water of their solutions.

Existing data[1] cover a range of temperatures from 0 to 110C, and compositions from 0 - 42 wt pct HCl, based on the data reported in References 2,3,4,5 & 6. They do not encompass the lower range of required service environmental temperatures below 0C to -55C. The Air Force Office of Scientific Research is sponsoring the University of Nevada, Mackay School of Mines, with Prof. Eugene Miller, Chem.&Met. Eng. Dept. as Principal Investigator, to measure these equilibrium vapor pressures for both liquid and frozen solutions in the range of 0 - 42 wt pct HCl and temperatures from 0 to -55C. This interim report summarizes the results of the program for the period 1 May 1977 to 31 August 1978.

EXPERIMENTAL

The experimental method used is an adaptation of one reported by Dunn and Rideal[3], distilling a small quantity of HCl and water from a relatively large volume of solution. The solution flask is immersed in a methylene chloride bath cooled by a two-stage mechanical refrigeration system. Temperatures are measured with a platinum resistance thermometer to 0.1C. Removal of air from the system is effected by a mechanical pump in series with a liquid nitrogen cryostat. Capacitance transduc-

ers with associated electronics are used to measure the total pressure with ± 1% accuracy. Samples of the solution are analyzed by electric conductivity measurements based on data from References 7 - 12 at 25C. Samples of the solution vapors are drawn from the vapor chamber into a mass spectrometer for analusis. Initially, the vapors were condensed in a dry ice or liquid nitogen trap for subsequent analysis. The condensation process was found to be too slow and has been abandoned in favor of the mass spectrometer. The latter is presently being incorporated into the experimental apparatus.

Hydrochloric acid solutions meeting the American Chemical Society standards have been used. No further purification of the solutions was attempted.

SUMMARY OF RESULTS

Total equilibrium pressures of two solutions, 19.9 and 36. wt. pct. liquid solutions have been measured todate for temperatures between 0 and -40C. The data are presented in Figure 1. Also shown are the accepted vapor pressures from 0 to 30C[11]. E.m.f. data of Akerlof and Teare[12] for 3 - 16 molal solutions and 0 - 50C were extrapolated to the conditions tested here. Then from the vapor pressures of pure HCl and water[13], and correcting for the difference in fugacity and pressure for HCl by the method of Lewis and Randall[14], extrapolated total pressures were derived. These are plotted in the Figure also.

Heat of vaporization values for the two solutions were calculated from the measured vapor pressures using the Clausius-Clapeyron equation. The derived values are given in Table I.

TABLE I

T, deg C	Heat of Vaporization, kcal/mol	
	19.9 wt pct	36. wt pct
-6.3		9.47
-7.2	9.24	
-17.4	10.67	
-17.7		9.80
-27.0	8.82	10.12
-36.1	8.51	
-36.3		8.62
-36.5		8.49

The agreement in total vapor pressure at 0C with the accepted values is within the reported accuracy of the data, providing confidence in the measured values for the lower temperatures. Extrapolations from Akerlof and Teare by the method described is reasonably good for the 19.9 wt pct HCl solution, but is unacceptable for the 36. wt pct solution. Simple extra-

polation of existing vapor pressure data would be more acceptable for the 36. wt pct solution.

FUTURE PLANS

Measurement of total solution vapor pressures and partial vapor pressures of hydrogen chloride and water for 0 - 42 wt pct hydrochloric acid liquid and solid solutions will be carried out at temperatures from 0 to -55C. Thermodynamic activities of the hydrogen chloride and water in solution and heats of vaporization will be derived.

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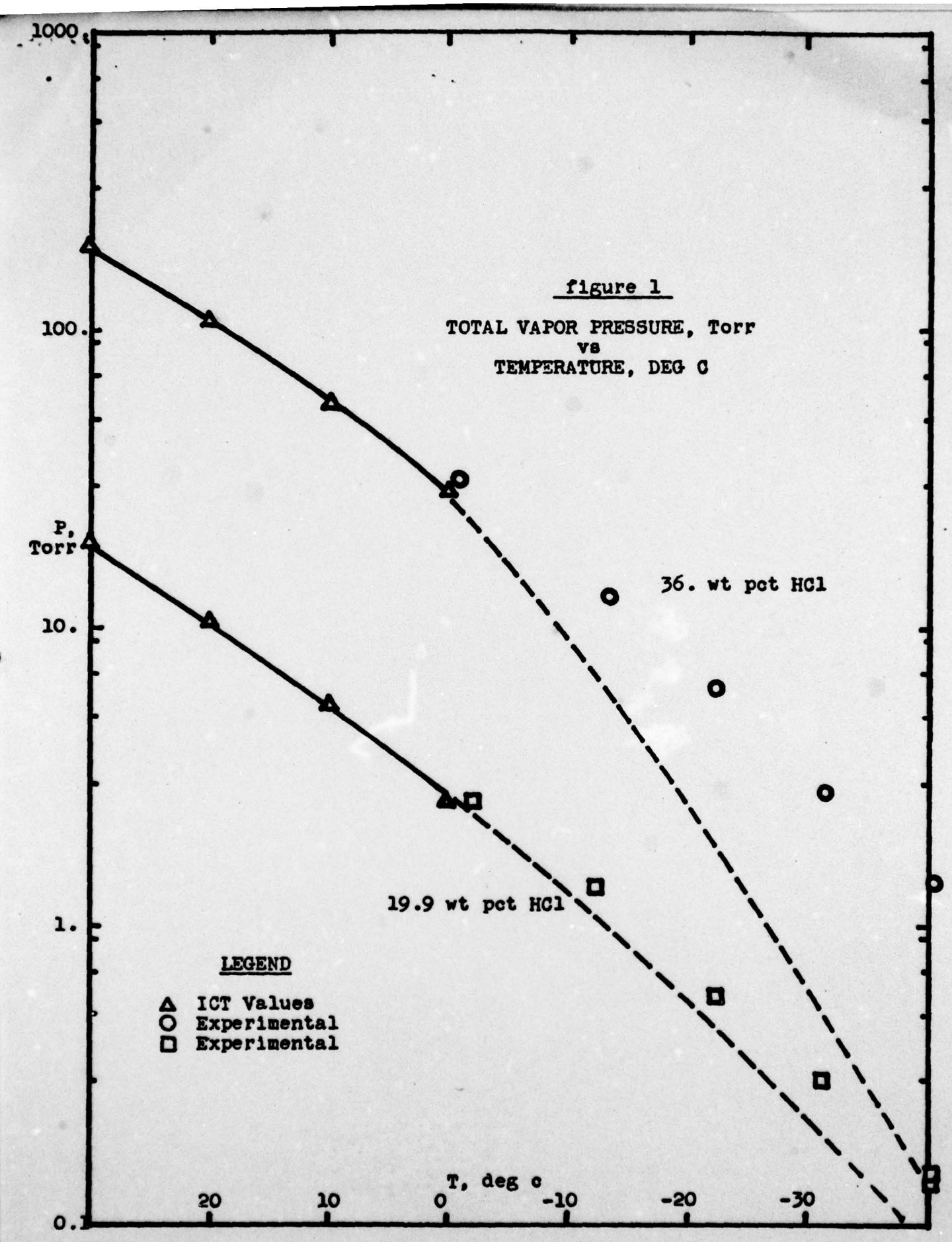
figure 1
TOTAL VAPOR PRESSURE, Torr
vs
TEMPERATURE, DEG C
1000.
100.
10.
1.
0.1
P, Torr
36. wt pct HCl
19.9 wt pct HCl
LEGEND
ICT Values
Experimental
Experimental
T, deg c
20
10
0
-10
-20
-30

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